* * * * * * * * * * * * * * STN Columbus * * * * * * * * * * * * * * *

FILE 'HOME' ENTERED AT 21:43:46 ON 11 JUN 2004

=> file registry
COST IN U.S. DOLLARS

	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.21	0.21

FILE 'REGISTRY' ENTERED AT 21:43:56 ON 11 JUN 2004
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
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STRUCTURE FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6
DICTIONARY FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2004

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=> s 323179-29-9/rn
L1 1 323179-29-9/RN

=> s 323179-30-2/rn
L2 1 323179-30-2/RN

=> s 323179-31-3/rn
L3 1 323179-31-3/RN

=> s l1 and l2 and l3
L4 0 L1 AND L2 AND L3

=> s l1 or l2 or l3
L5 3 L1 OR L2 OR L3

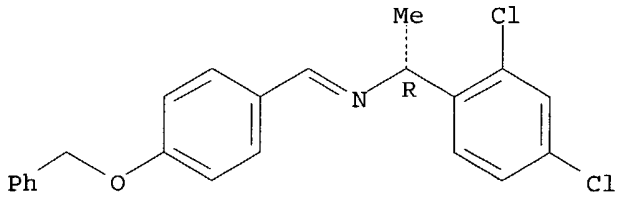
=> d 1-3 l5

L5 ANSWER 1 OF 3 REGISTRY COPYRIGHT 2004 ACS on STN
RN **323179-31-3** REGISTRY
CN Benzenemethanamine, 2,4-dichloro-α-methyl-N-[[4-(phenylmethoxy)phenyl]methylene]-, (αR)- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C22 H19 Cl2 N O
SR CA
LC STN Files: CA, CAPLUS, USPAT2, USPATFULL
DT.CA CAplus document type: Patent

10603941

RL.P Roles from patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry unknown.

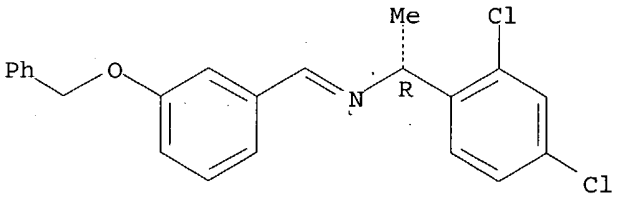


PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L5 ANSWER 2 OF 3 REGISTRY COPYRIGHT 2004 ACS on STN
RN **323179-30-2** REGISTRY
CN Benzenemethanamine, 2,4-dichloro-α-methyl-N-[[3-(phenylmethoxy)phenyl]methylene]-, (αR)- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C22 H19 Cl2 N O
SR CA
LC STN Files: CA, CAPLUS, USPAT2, USPATFULL
DT.CA CAplus document type: Patent
RL.P Roles from patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry unknown.



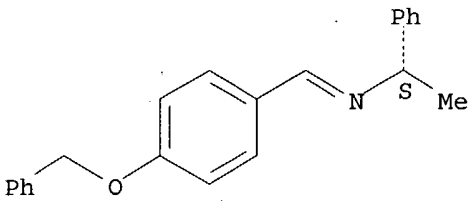
PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L5 ANSWER 3 OF 3 REGISTRY COPYRIGHT 2004 ACS on STN
RN **323179-29-9** REGISTRY
CN Benzenemethanamine, α-methyl-N-[[4-(phenylmethoxy)phenyl]methylene]-, (αS)- (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C22 H21 N O
SR CA
LC STN Files: CA, CAPLUS, USPAT2, USPATFULL
DT.CA CAplus document type: Patent
RL.P Roles from patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry unknown.

10603941



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	6.57	6.78

FILE 'CAPLUS' ENTERED AT 21:45:43 ON 11 JUN 2004
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FILE COVERS 1907 - 11 Jun 2004 VOL 140 ISS 25
FILE LAST UPDATED: 10 Jun 2004 (20040610/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l5
L6 1 L5

=> d 1 bib abs l5
YOU HAVE REQUESTED DATA FROM FILE 'REGISTRY' - CONTINUE? (Y)/N:n

=> d bib abs l6

L6 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2001:98451 CAPLUS
DN 134:147313
TI Preparation of optically active 3,3,3-trifluoro-2-hydroxy-2-methylpropionic acid and salts thereof.
IN Oikawa, Miyuki; Ushio, Hideki; Kurimoto, Isao; Higashi, Takayuki
PA Sumitomo Chemical Company, Limited, Japan
SO Eur. Pat. Appl., 28 pp.

10603941

CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 1074539	A2	20010207	EP 2000-116789	20000803
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO				
	JP 2001106661	A2	20010417	JP 2000-224998	20000726
	JP 2001213843	A2	20010807	JP 2000-232771	20000801
	US 6403832	B1	20020611	US 2000-632804	20000804
	US 2002143212	A1	20021003	US 2002-147966	20020520
	US 6653507	B2	20031125		
	US 2003232886	A1	20031218	US 2003-603941	20030626
PRAI	JP 1999-221065	A	19990804		
	JP 1999-333924	A	19991125		
	US 2000-632804	A3	20000804		
	US 2002-147966	A3	20020520		

OS MARPAT 134:147313

AB F3C(Me)C*(OH)CO2- H2N+(R3)CH*R1R2 [R1 = alkyl, hydroxyalkyl, (substituted) aryl; R2 = alkyl, hydroxyalkyl, (substituted) aralkyl; R3 = H, alkyl, hydroxyalkyl, cyclohexyl, (substituted) aralkyl; starred atoms are independently in the S- or R-configuration; R1 ≠ R2; when R1 = Ph and R2 = Me, then R3 ≠ H], and (S)- and (R)-3,3,3-trifluoro-2-hydroxy-2-methylpropionic acid, were prepared Thus, racemic 3,3,3-trifluoro-2-hydroxy-2-methylpropionic acid in MeOCMe3 at 55° was treated with (S)-N-benzyl-1-phenyl-2-(p-tolyl)ethylamine in MeOCMe3 followed by cooling to 20° over 3 h to give (R)-3,3,3-trifluoro-2-hydroxy-2-methylpropionic acid (S)-N-benzyl-1-phenyl-2-(p-tolyl)ethylamine salt in 95% enantiomeric excess. This was stirred with aqueous NaOH and MeOCMe3 followed by separation of the layers and treatment of the aqueous layer with aqueous HCl and MeOCMe3 followed by isolation of the MeOCMe3 layer and concentration to give (R)-3,3,3-trifluoro-2-hydroxy-2-methylpropionic acid in 95% enantiomeric excess.

10603941

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LOGINID:ssspta1623hrr

PASSWORD:
TERMINAL (ENTER 1, 2, 3, OR ?):2

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NEWS	1		Web Page URLs for STN Seminar Schedule - N. America
NEWS	2		"Ask CAS" for self-help around the clock
NEWS	3	JAN 27	Source of Registration (SR) information in REGISTRY updated and searchable
NEWS	4	JAN 27	A new search aid, the Company Name Thesaurus, available in CA/CAplus
NEWS	5	FEB 05	German (DE) application and patent publication number format changes
NEWS	6	MAR 03	MEDLINE and LMEDLINE reloaded
NEWS	7	MAR 03	MEDLINE file segment of TOXCENTER reloaded
NEWS	8	MAR 03	FRANCEPAT now available on STN
NEWS	9	MAR 29	Pharmaceutical Substances (PS) now available on STN
NEWS	10	MAR 29	WPIFV now available on STN
NEWS	11	MAR 29	New monthly current-awareness alert (SDI) frequency in RAPRA
NEWS	12	APR 26	PROMT: New display field available
NEWS	13	APR 26	IFIPAT/IFIUDB/IFICDB: New super search and display field available
NEWS	14	APR 26	LITALERT now available on STN
NEWS	15	APR 27	NLDB: New search and display fields available
NEWS	16	May 10	PROUSDDR now available on STN
NEWS	17	May 19	PROUSDDR: One FREE connect hour, per account, in both May and June 2004
NEWS	18	May 12	EXTEND option available in structure searching
NEWS	19	May 12	Polymer links for the POLYLINK command completed in REGISTRY
NEWS	20	May 17	FRFULL now available on STN
NEWS	21	May 27	STN User Update to be held June 7 and June 8 at the SLA 2004 Conference
NEWS	22	May 27	New UPM (Update Code Maximum) field for more efficient patent SDIs in CAplus
NEWS	23	May 27	CAplus super roles and document types searchable in REGISTRY
NEWS	24	May 27	Explore APOLLIT with free connect time in June 2004

NEWS EXPRESS	MARCH 31 CURRENT WINDOWS VERSION IS V7.00A, CURRENT MACINTOSH VERSION IS V6.0c(ENG) AND V6.0Jc(JP), AND CURRENT DISCOVER FILE IS DATED 26 APRIL 2004
NEWS HOURS	STN Operating Hours Plus Help Desk Availability
NEWS INTER	General Internet Information
NEWS LOGIN	Welcome Banner and News Items
NEWS PHONE	Direct Dial and Telecommunication Network Access to STN
NEWS WWW	CAS World Wide Web Site (general information)

Enter NEWS followed by the item number or name to see news on that specific topic.

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FILE 'HOME' ENTERED AT 21:43:46 ON 11 JUN 2004

=> file registry

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.21	0.21

FILE 'REGISTRY' ENTERED AT 21:43:56 ON 11 JUN 2004

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6
DICTIONARY FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2004

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. For more information enter HELP PROP at an arrow prompt in the file or refer to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

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=> s 323179-29-9/rn
L1            1 323179-29-9/RN

=> s 323179-30-2/rn
L2            1 323179-30-2/RN

=> s 323179-31-3/rn
L3            1 323179-31-3/RN

=> s l1 and l2 and l3
L4            0 L1 AND L2 AND L3

=> s l1 or l2 or l3
L5            3 L1 OR L2 OR L3

=> d 1-3 l5

L5   ANSWER 1 OF 3  REGISTRY  COPYRIGHT 2004 ACS on STN
RN   323179-31-3  REGISTRY
CN   Benzenemethanamine, 2,4-dichloro-α-methyl-N-[[4-
     (phenylmethoxy)phenyl]methylene]-, (αR)- (9CI)  (CA INDEX NAME)
FS   STEREOSEARCH
MF   C22 H19 Cl2 N O
SR   CA
LC   STN Files:   CA, CAPLUS, USPAT2, USPATFULL
DT.CA  CAplus document type:  Patent
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10603941

FILE 'REGISTRY' ENTERED AT 18:49:06 ON 11 JUN 2004
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Property values tagged with IC are from the ZIC/VINITI data file
provided by InfoChem.

STRUCTURE FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6
DICTIONARY FILE UPDATES: 10 JUN 2004 HIGHEST RN 691838-95-6

TSCA INFORMATION NOW CURRENT THROUGH JANUARY 6, 2004

Please note that search-term pricing does apply when
conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

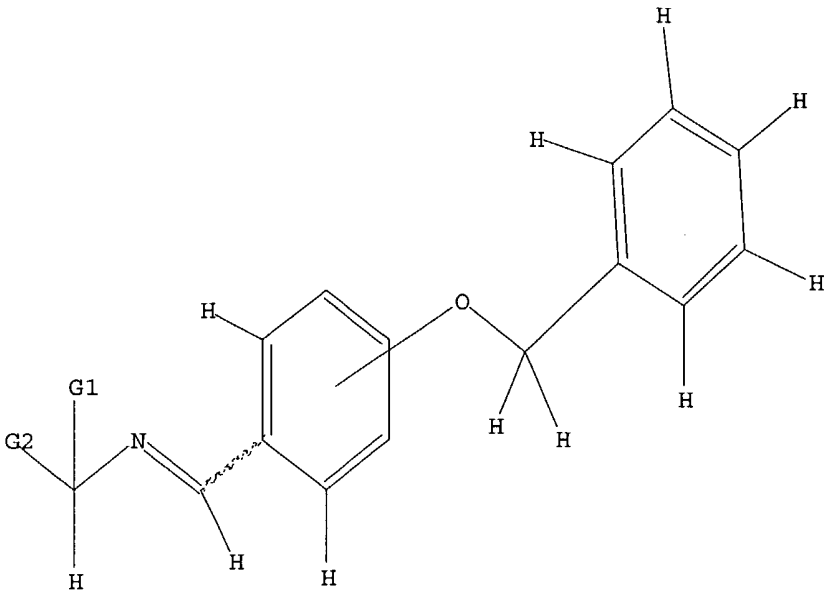
Experimental and calculated property data are now available. For more
information enter HELP PROP at an arrow prompt in the file or refer
to the file summary sheet on the web at:
http://www.cas.org/ONLINE/DBSS/registryss.html

=>
Uploading C:\STNEXP4\QUERIES\10603941-5.str

L7 STRUCTURE UPLOADED

=> dl7
DL7 IS NOT A RECOGNIZED COMMAND
The previous command name entered was not recognized by the system.
For a list of commands available to you in the current file, enter
"HELP COMMANDS" at an arrow prompt (=>).

=> d l7
L7 HAS NO ANSWERS
L7 STR



G1 Cy,C,Me

G2 Ak,O,NO2,Cl,Br,F,I

10603941

Structure attributes must be viewed using STN Express query preparation.

=> s l7 full
FULL SEARCH INITIATED 18:49:42 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 977562 TO ITERATE

40.9% PROCESSED 400000 ITERATIONS 2 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.15

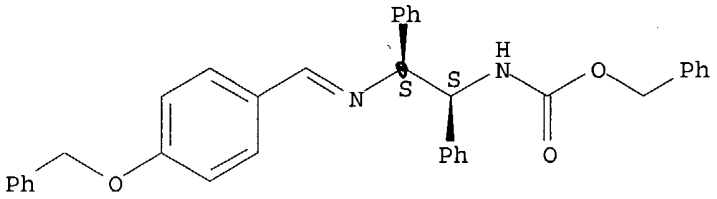
FULL FILE PROJECTIONS: ONLINE **INCOMPLETE**
BATCH **INCOMPLETE**
PROJECTED ITERATIONS: 977562 TO 977562
PROJECTED ANSWERS: 2 TO 10

L8 2 SEA SSS FUL L7

=> d l8

L8 ANSWER 1 OF 2 REGISTRY COPYRIGHT 2004 ACS on STN
RN 442669-49-0 REGISTRY
CN Carbamic acid, [(1S,2S)-1,2-diphenyl-2-[[[4-(phenylmethoxy)phenyl]methylene]amino]ethyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C36 H32 N2 O3
SR CA
LC STN Files: CA, CAPLUS, CASREACT
DT.CA CAplus document type: Patent
RL.P Roles from patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry unknown.



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

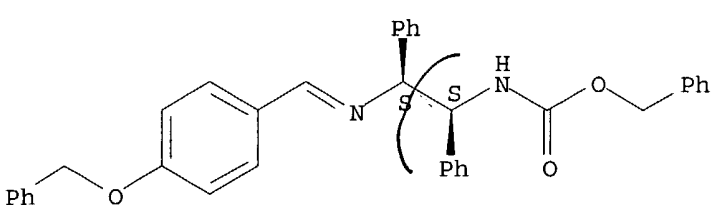
=> d 1-2 l8

L8 ANSWER 1 OF 2 REGISTRY COPYRIGHT 2004 ACS on STN
RN 442669-49-0 REGISTRY
CN Carbamic acid, [(1S,2S)-1,2-diphenyl-2-[[[4-(phenylmethoxy)phenyl]methylene]amino]ethyl]-, phenylmethyl ester (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C36 H32 N2 O3
SR CA
LC STN Files: CA, CAPLUS, CASREACT
DT.CA CAplus document type: Patent

10603941

RL.P Roles from patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry unknown.



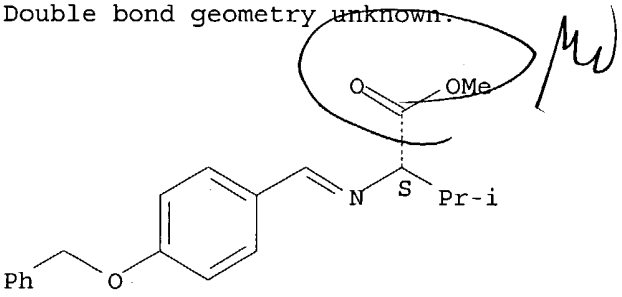
MW alkyl group. or aralkyl

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

L8 ANSWER 2 OF 2 REGISTRY COPYRIGHT 2004 ACS on STN
RN 405297-09-8 REGISTRY
CN L-Valine, N-[[4-(phenylmethoxy)phenyl]methylene]-, methyl ester (9CI) (CA INDEX NAME)
FS STEREOSEARCH
MF C20 H23 N O3
SR CA
LC STN Files: CA, CAPLUS
DT.CA CAplus document type: Journal
RL.NP Roles from non-patents: PREP (Preparation); RACT (Reactant or reagent)

Absolute stereochemistry.
Double bond geometry ~~unknown~~.



MW

PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

1 REFERENCES IN FILE CA (1907 TO DATE)
1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> file caplus

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	161.15	1165.43

FILE 'CAPLUS' ENTERED AT 18:50:24 ON 11 JUN 2004
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FILE COVERS 1907 - 11 Jun 2004 VOL 140 ISS 25
FILE LAST UPDATED: 10 Jun 2004 (20040610/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s l8
L9 2 L8

=> d 1-2 bib abs l9

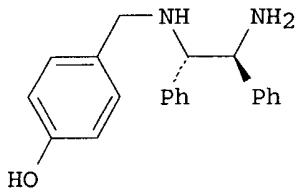
L9 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2002:539640 CAPLUS
DN 137:118618
TI Preparation of ruthenium compounds as asymmetric hydrogenation catalysts and diamine ligands, and process for producing optically active β-amino-alcohol from α-aminocarbonyl compounds
IN Sato, Daisuke; Ooka, Hirohito; Inoue, Tsutomu
PA Nippon Soda Co., Ltd., Japan
SO PCT Int. Appl., 41 pp.
CODEN: PIXXD2
DT Patent
LA Japanese
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2002055477	A1	20020718	WO 2002-JP191	20020115

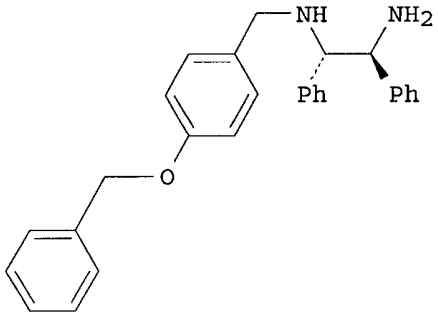
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG

PRAI JP 2001-6258 A 20010115
OS CASREACT 137:118618; MARPAT 137:118618
GI

10603941



I



II

AB Disclosed are ruthenium-phosphine-diamine complexes which are useful as catalysts for asym. hydrogenation, diamine ligands, and a process for highly stereoselectively producing optically active alcs. in high yield. The process comprises using a ruthenium compound represented by the general formula Ru(Px)n1[DIAMINE](X)(Y) [wherein Px represents a phosphine ligand; DIAMINE represents an optically active diamine represented by the general formula R1R2C*(NHR5)-(A)-R3R4C*(NH2) [wherein R1 to R4 each independently represents hydrogen, optionally substituted alkyl, alkenyl, cycloalkyl, aralkyl, or aryl; A represents optionally substituted C1-3 alkylene optionally containing an ether bond, optionally substituted C3-8 cycloalkylene, arylene, or divalent heterocyclic ring, or a single bond; R5 represents optionally substituted alkyl, optionally substituted aralkyl, or optionally substituted aryl; and C* represent s asym. carbon]; X and Y each independently represents an anion; and n1 is an integer of 1 or 2] as a catalyst for asym. hydrogenation to produce a β-amino alc. from an α-aminocarbonyl compound Thus, condensation of (1S,2S)-N-benzyloxycarbonyl-1,2-diphenyl-1,2-ethanediamine with 4-benzyloxybenzaldehyde in CHCl3 at room temperature for 19 h gave 84% (1S,2S)-N-(4-benzyloxybenzylidene)-N'-benzyloxycarbonyl-1,2-diphenyl-1,2-ethanediamine which underwent hydrogenation over 5% Pd-C in a 1:1 mixture of MeOH and THF (30 mL) at room temperature for 18 h to give 48% (1S,2S)-N-(4-hydroxybenzyl)-1,2-diphenyl-1,2-ethanediamine (I). Treatment of I with NaH in DMF at room temperature for 2 h followed by benzylation with benzyl bromide at room temperature for 4 h gave 53% (1S,2S)-N-(4-benzyloxybenzyl)-1,2-diphenyl-1,2-ethanediamine (II). [[(S)-tol-Binap]RuCl2](DMF)n [tol-Binap = 2,2'-bis[di(p-tolyl)phosphino]-1,1'-dinaphthyl] (5 mg), 2 mg II, 0.5 M Me3COK/2-propanol (0.3 mL), and a solution of 134 mg 1-phenyl-2-(N-methyl-N-benzoylamino)propan-1-one in 3 mL 2-propanol were added to an autoclave, degassed, and pressurized with H to 12 atm, and stirred at room temperature for 2 h to give 100% (1S,2S)-1-phenyl-2-(N-methyl-N-benzoylamino)-1-propanol (89% ee).

RE.CNT 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L9 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2004 ACS on STN
AN 2002:32239 CAPLUS
DN 136:263549
TI Synthesis of novel chiral monomers by means of Umani-Ronchi-Savoia

10603941

allylation and their polymerization

AU Itsuno, Shinichi; El-Shehawy, Ashraf A.
CS Department of Materials Science, Toyohashi University of Technology, Toyohashi, 441-8580, Japan

SO Polymers for Advanced Technologies (2001), 12(11-12), 670-679
CODEN: PADTE5; ISSN: 1042-7147
PB John Wiley & Sons Ltd.
DT Journal
LA English

AB Umani-Ronchi-Savoin allylation is one of the most successful and useful methods for the preparation of optically pure secondary amines bearing two stereogenic centers at both α-positions. We have prepared novel chiral amine monomers by means of this methodol. as a key step of the synthesis. Diastereoselective allylation of chiral imines (3-5) derived from (S)-valine gave optically pure secondary amines 6. Hydrogenation of the allylic group followed by introduction of a polymerizable 4-vinylphenyl group led to enantiopure monomer 9. Prenylzinc reagents were also found to react with the imines to yield the corresponding optically pure amines 7. Since prenyl addition product does not inhibit the radical polymerization, chiral monomers 7b, 7d could be prepared directly by prenylzinc addition to imine having a polymerizable group. These chiral monomers were easily polymerized with styrene under radical polymerization conditions.

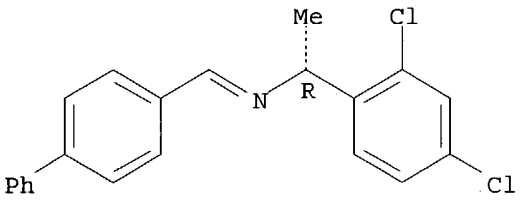
RE.CNT 18 THERE ARE 18 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMA

preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation of dibenzylamines, their intermediate imines, and their use in optical resolution)

RN 323179-32-4 HCAPLUS

CN Benzenemethanamine, N-([1,1'-biphenyl]-4-ylmethylene)-2,4-dichloro-α-methyl-, (αR)- (9CI) (CA INDEX NAME)

Absolute stereochemistry.
Double bond geometry unknown.



L21 ANSWER 2 OF 3 HCAPLUS COPYRIGHT 2004 ACS on STN

AN 2001:512467 HCAPLUS

DN 135:242611

TI Preparation of dendritic and non-dendritic styryl-substituted Salens for cross-linking suspension copolymerization with styrene and multiple use of the corresponding Mn and Cr complexes in enantioselective epoxidations and hetero-Diels-Alder reactions

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SO Chemistry--A European Journal (2001), 7(13), 2873-2887
CODEN: CEUJED; ISSN: 0947-6539

PB Wiley-VCH Verlag GmbH

DT Journal

LA English

AB Following work with TAD-DOLs and BINOLs, we have now prepared Salen derivs. (2, 3, 14, 15, 18, 19, 20, 21) carrying two to eight styryl groups for crosslinking copolymn. with styrene. The Salen cores are either derived from (R,R)-diphenyl ethylene diamine (3, 15, 19, 21) or from (R,R)-cyclohexane diamine (2, 14, 18, 20). The styryl groups are attached to the salicylic aldehyde moieties, using Suzuki (cf. 1) or Sonogashira cross-coupling (cf. 11), and/or phenolic etherification (cf. 5, 7) with dendritic styryl-substituted Frechet-type benzylic branch bromides. Subsequent condensation with the diamines provides the chiral Salens. Corresponding Salens lacking the peripheral vinyl groups (cf. 12, 13, 16, 17) were also prepared for comparison of catalytic activities in homogeneous solution with those in polystyrene. Crosslinking radical suspension copolymn. of styrene and styryl Salens, following a procedure by Itsuno and Frechet, gave beads (ca. 400 μm diameter) which were loaded with Mn or Cr (ca. 0.2 mmol of complex per g of polymer), with more than 95% of the Salen incorporated being actually accessible for complexation (by elemental anal.). The polymer-bound Mn and Cr complexes were used as catalysts for epoxidns. of six phenyl-substituted olefins (m-CPBA/NMO; products 22a-f), and for dihydropyranone formation from the Danishefsky diene and aldehydes (PhCHO, C5H11CHO, C6H11CHO, products 23a-c). There are several remarkable features of the novel immobilized Salens: (i) The dendritic branches do not slow down the catalytic activity of the complexes in solution; (ii) the reactions with Salen catalysts incorporated in polystyrene give products of essentially the same enantiopurity as those observed in homogeneous solution with the dendritically substituted or

with the original Jacobsen-Katsuki complexes; (iii) some Mn-loaded beads have been stored for a year, without loss of activity; (iv) especially the biphenyl- and acetylene-linked Salen polymers (p-2, -3, -20, -21, Figure 2, 3) give Mn complexes of excellent performance: after ten uses (without re-charging with Mn!) there is no loss of enantioselectivity or degree of conversion under the standard conditions.

IT **360785-08-6P 360785-12-2P 360785-14-4P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(crosslinking agent; preparation of dendritic and non-dendritic styryl-substituted salens)

IT **360785-10-0P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(epoxidn. catalyst ligand; preparation of dendritic and non-dendritic styryl-substituted salens)

IT **360785-06-4P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(epoxidn. catalyst ligand; preparation of dendritic and non-dendritic styryl-substituted salens)

IT **360785-06-4DP**, manganese complexes **360785-10-0DP**, manganese complexes
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)
(epoxidn. catalyst; preparation of dendritic and non-dendritic styryl-substituted salen-crosslinked polystyrene Mn and Cr complexes and their use as catalysts in enantioselective epoxidns. and hetero-Diels-Alder reactions)

IT **360785-08-6P**
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(crosslinking agent; preparation of dendritic and non-dendritic styryl-substituted salens)

RN 360785-08-6 HCAPLUS

CN Phenol, 2,2'-[[(1R,2R)-1,2-diphenyl-1,2-ethanediyl]bis[(Z)-nitrilomethylidyne]]bis[4-[[3,5-bis[(4-ethenylphenyl)methoxy]phenyl]methoxy]-6-(1,1-dimethylethyl)- (9CI) (CA INDEX NAME)

Absolute stereochemistry. Rotation (-).
Double bond geometry as shown.